

**ELECTROLYTES FOR LOW TEMPERATURE LITHIUM BATTERIES  
BASED ON TERNARY MIXTURES OF ALIPHATIC CARBONATES**

*M. C. Smart, B. V. Ratnakumar\* and S. Surampudi*

*Jet Propulsion Laboratory, California Institute of Technology*

*4800 Oak Grove Dr., Pasadena, California 91109*

*\* To whom all correspondence may be addressed.*

## 1.0 INTRODUCTION

The success of rechargeable lithium ion batteries may be largely attributed to the surface films on the carbon anodes, which provide the anodes with adequate protection against continued reaction with electrolyte while permitting charge transfer. The surface films apparently permit adequate conduction of lithium ions (hence termed as solid electrolyte interface)<sup>1</sup> without any breakdown, unlike the passive films on the reactive (valve) metals. Among the various types of non-aqueous solvents studied, alkyl carbonates such as ethylene, propylene, dimethyl and diethyl carbonates or combinations thereof have emerged as the most appropriate solvents for carbonaceous anodes.<sup>2,3</sup> Their reactions with carbon anodes during the first lithiation cycle, termed as staging, reportedly form surface films of mostly lithium carbonate and lithium alkoxide species.<sup>4</sup> Such surface films have provided good stability to the anodes towards electrolyte reduction in the subsequent lithium intercalation - deintercalation cycles, which may be in the range of 1000-2000 cycles.

One of the disadvantages associated with the use of the carbonate-based solvents is evident from poor performance of the cells at low temperatures. Due to relatively high freezing points of some of these solvents (EC, DMC), conductivities of the corresponding electrolyte solutions fall rapidly at low temperatures. As a result, the performance of the lithium ion cells with state-of-art electrolytes based on carbonate solvents is limited to -20°C (could be lower with PC-based electrolytes used with coke anodes). One of the current practices to alleviate this is to use ternary or quaternary mixtures of solvents, the co-solvents being selected based on several critical properties, such as: high dielectric constant, low viscosity, adequate coordination behavior, as well as appropriate liquid ranges and salt solubilities in the medium. Our approach to designing highly conductive electrolyte solutions at low temperature has focused upon mixtures with small proportions of ethylene carbonate with suitable solvent additives to mainly to reduce the freezing point and the viscosity of the electrolyte solution at low temperatures. It is generally believed that multi-component systems are more tenable, since their physicochemical properties

(i.e., dielectric constant, viscosity, liquid range, coordination properties, and overall stability) can be better tailored and mixed solvent systems are known to produce solutions of higher conductivity than single solvent systems due to a disordering effect in the lithium ion coordination behavior of the solvent medium. This approach has recently led to the development of new electrolyte formulations for low temperature applications, with quaternary additions of formates, acetates, cyclic and aliphatic ethers, lactones, as well as other carbonates, such as diethyl carbonate (DEC).<sup>5</sup>

In addition to the improved low temperature, our applications, e.g., Rover and Lander in NASA's Mars Exploration missions, require adequate stability and cycle life at ambient temperatures as well. The stability of some of the above co-solvents is still to be established, especially in the quaternary mixtures as above. As an alternate, our interim approach is based on continuing entirely with the carbonate-based solvents that have the desired stability at room temperatures and explore means of enhancing their low temperature performance.

In designing highly conductive electrolytes it is necessary to consider a number of important parameters, such as the dielectric constant of the medium, viscosity, Lewis acid-base coordination behavior, as well as the appropriate liquid ranges and salt solubilities of the systems. In addition, they need to have (i) good electrochemical stability over a wide voltage window (0 to 4.5V), (ii) ability to form thin, stable passivating films at the carbonaceous anode electrode, and (iii) good thermal and chemical stability. The relevant physicochemical properties of typical organic carbonate solvents employed in lithium-ion technology are shown in Table 1.

An effective way to improve the low temperature conductivity of the electrolyte solution is to extend the liquid range and decrease the viscosity of the solvent system used. As may be seen from the above Table, with increasing size of the alkyl group, i.e., from methyl to ethyl, there is a decrease in the viscosity, density and freezing temperature, all of which aid in an improved ionic conductivity at low temperatures. On the other hand, the

polarizability of the solvents also decreases in the same order, as evident from lower dielectric constants. It is thus clear that the higher homologues of the alkyl carbonate may not facilitate much salt solubility by themselves. However, in the mixtures containing considerable proportions of EC (or PC), the higher carbonate additions can enhance ionic conductivity due to reduced viscosity and freezing temperature. In this paper, therefore, we carried out a detailed evaluation of the performance of electrolyte solutions with varying amounts of DMC and DEC additions to EC-based solutions. Specifically, the electrolyte mixtures investigated include  $\text{LiPF}_6$  dissolved in 1) EC:DMC 30:70, 2) EC:DEC 30:70 and 3) EC:DMC:DEC: 1:1:1, respectively, and would illustrate the effects of the ratio of DMC:DEC co-solvents in EC-based electrolyte.

## 2.0 EXPERIMENTAL

Conductivities of the electrolytes were measured using an Orion conductivity cell with platinum electrodes, whose cell constant was determined using standard KCl solution. Conductivity values were estimated from AC impedance values obtained as described below. Electrochemical measurements were made in prismatic, three-electrode, glass cells. Graphite electrodes were fabricated by spray-coating copper foil with the mixture of active material (typically Alfa graphite unless mentioned otherwise) and PVDF binder. Cathodes were made in a similar fashion with Al foil substrates and Alfa lithiated cobalt oxide, mixed with acetylene black as conductive diluent. Electrolytes used were of battery grade, obtained from Mitsubishi chemicals. Porous polypropylene (Celgard 2500) was used as the separator in the cells.

Electrodes of both graphite and lithiated cobalt oxide were prepared by spraying mixtures of active material and PVDF (and conductive diluent in the latter case) dispersed in cyclopentanone onto copper and aluminum foil substrates, respectively. Subsequently, electrodes were compressed and dried under vacuum. Basic electrochemical studies such as AC and DC polarization studies were carried out in prismatic, O-ring sealed, glass cells

with lithium counter and reference electrodes. Sealed cells of AA size (400-500 mAh) were fabricated by Wilson Greatbatch Ltd., Clarence, NY with the specified components and design parameters such as electrode loading and cell balance.

Electrochemical measurements were carried out with an EG&G Potentiostat/Galvanaostat (model 273) and Solartron Frequency Response Analyzer (model 1255) interfaced with an IBM PC, using Softcorr 352 and Electrochemical Impedance Spectroscopy (398) software. Cycling of the cells was carried out with an Arbin Battery Cycler. Cells were charged at constant current to a cut-off voltage of 4.1 V (or 0.025 V vs. Li in the case of graphite half-cells), followed by tapered current for an additional three hours (or to a current limit of C/50) and discharged at constant current to 3.0 V (or 1.0 V vs. Li for graphite).

### **3.0 RESULTS AND DISCUSSION**

#### **3.1 Electrolyte Conductivity**

Ionic conductivities of the electrolyte solutions containing 1.0 M LiPF<sub>6</sub> in aliphatic carbonate solvent mixtures, i.e., EC/DMC (30:70), EC/DEC (30:70) and the equi-volume ternary mixture (EC:DMC:DEC) are shown in Fig. 1. As may be seen from the figure, solutions with high DMC content have higher conductivity at room temperature compared to DEC-based solutions, with the ternary mixture falling in between. At low temperatures, on the other hand, the conductivity falls rapidly in solutions with high DMC content due to its high freezing temperature. The corresponding DEC electrolyte exhibits low conductivity at temperatures above -20°C, as may be expected from its higher viscosity and lower dielectric constant. Nevertheless, at temperatures below -20°C, it exhibits improved conductivity compared to the DMC-based electrolyte. Interestingly, the equi-volume ternary mixture, shows conductivities superior to either the DMC or DEC-based electrolytes, possibly due to a combination of depressed freezing temperature (compared to DMC-based electrolyte) and lower viscosity (compared to DEC-based

electrolyte). The improved conductivity of the ternary system over the binary electrolytes at low temperatures may thus be attributed to the synergistic effects of EC (possesses good coordinating ability and high dielectric constant), DEC (low melting point), and DMC (low viscosity) present in appropriate proportions and the possibility of forming more disordered coordination complexes in mixed solvent systems.

### 3.2 Reversible and Irreversible Capacities

It is well known that during the initial charge – discharge (formation) cycles (typically five), there is a differential in the intercalated and de-intercalated capacities, termed as ‘irreversible capacity’. This is mostly attributed to the formation of protective surface films on graphite, and hence is a strong function of the nature of electrolyte. The profiles of lithium intercalation/de-intercalation in the three electrolytes under study are shown in Fig. 2.

Typically, lithium intercalated at potentials  $\geq 200$  mV vs. Li is utilized in the formation of surface film on the graphite anode and thus is not realizable in the subsequent delithiation. As may be seen from the figure, DMC-based electrolyte facilitates rapid film formation compared to DEC-based electrolyte, evidenced by a sharper fall in the potential during the first lithiation (staging of graphite). Accordingly, its irreversible capacity is expected to be lower. The ternary system behaves similar to DMC electrolyte in terms of staging. During subsequent delithiation, the electrode potentials are low for the ternary electrolyte compared to DEC electrolyte (or even DMC electrolyte), which may be due to more facile kinetics in the ternary system, as discussed below.

The reversible and irreversible capacities of graphite in these three electrolytes were determined in half-cells as well as in several experimental 400 mAh Li ion cells. Typical values of these capacities observed in the sealed AA cells (400 mAh) are listed in Table 2. The reversible capacities represent the values after five charge-discharge cycles, whereas the irreversible capacities were cumulative during these formation cycles. As

illustrated in Table 2, the cells containing electrolytes consisting of 1.0M LiPF<sub>6</sub> EC + DMC (30:70) display the lowest irreversible capacities of the series studied, whereas the cells with 1.0M LiPF<sub>6</sub> EC + DEC (30:70) displayed the highest irreversible capacities, which is consistent with their intercalation potentials (Fig. 2) in the first lithiation. This trend suggests that DMC has inherently greater stability compared with DEC when placed in contact with lithiated carbon, as also observed earlier.<sup>6</sup> Cells containing EC + DEC + DMC (1:1:1) displayed irreversible capacity values which are intermediary, the cells containing EC + DEC + DMC (1:1:1) displayed behavior consistent with the fact that it is a mixture containing both DMC (less reactive) and DEC (more reactive).

### 3.3 Basic Electrochemical Studies

The surface films formed on the carbon anodes generally prevent further reaction of the electrolyte (and thus ensure durability to the cell) but also facilitate lithium intercalation-deintercalation processes. Since the latter processes occur on the film-covered electrodes, the characteristics of the films, such as conductivity and thickness would dictate the kinetics of intercalation and deintercalation of lithium into graphite. In order to obtain a quantitative understanding of the latter, basic electrochemical studies such as DC micro- and Tafel polarization and *ac* impedance studies were carried out with graphite electrodes in three different electrolytes in half-cells.

#### 3.3.1 DC Micropolarization

At low overpotentials ( $\ll RT/\alpha nF$ , where  $\alpha$  is the transfer coefficient,  $n$  is the number of equivalents/mol and  $R$  and  $F$  are the gas and Faraday constants, respectively), the electrochemical rate equation could be linearized, implying that there is a linear relationship between current and overpotential. Fig. 3 shows typical micropolarization plots of graphite in the three electrolytes at 25°C. These curves were obtained under potentiodynamic conditions at scan rates of 0.02 mV/s. From the slopes of these linear plots, the polarization resistance or the exchange current density could be calculated.

Corrections could be made for the ohmic effects from the surface films as obtained from ac impedance data as well as for the mass transfer effects evident in Tafel polarizations.

Such polarization experiments were performed at different (low) temperatures as well, i.e., at 0 and  $-20^{\circ}\text{C}$ . Expectedly, at low temperatures, the curves show increasing polarization resistance. Exchange current densities calculated from the micropolarization curves are plotted against temperature for the three electrolyte solutions (Table 3). It is clear from the Table that the kinetics of Li intercalation are more facile in the ternary solvent mixture, especially at low temperatures. In other words, the surface films formed on graphite in the ternary mixture facilitate Li ion diffusion and/or charge transfer compared to the films in the binary mixtures, especially in the DMC-based electrolyte.

### 3.3.2 Tafel Polarization

With the aim of determining the effects of mass transfer, i.e., kinetics of Li diffusion across the surface films on the charge transfer kinetics, Tafel polarization measurements were carried out in the above electrolytes. These measurements were made at slow scan rates of 0.5 mV/s to provide near-steady state conditions and yet with minimal changes in the state of charge of the electrode or its surface conditions.

The Tafel plots (Fig. 4) indicate the relatively slower kinetics in the DMC-based electrolyte. Because of this, there is a distinct Tafel (linearity between potential and logarithm of current) regime, whereas with the DEC-based and ternary mixture, there is evidence for mass transfer effects setting in earlier. The limiting currents may be related to the slow solid-state diffusion of Li in across the surface layer and/or graphite. The diffusion limiting current, measured at an overpotential of 400 mV is the highest for the ternary mixture followed by DEC. Using the limiting current thus measured, the Tafel plots have been corrected for the mass transfer effects, by plotting logarithm of  $I/(1-I/I_{\text{lim}})$  against the electrode potential. The corrected Tafel plots are fairly linear. The rate parameters for the deintercalation of lithium, i.e., exchange current density and transfer



coefficients were calculated from the intercept and slope of the corrected anodic Tafel plots, respectively. The exchange current density is the least for the DMC-based electrolyte as also observed in the micropolarization. Similar Tafel measurements were made at low temperatures also, i.e., -0 and -20°C. The exchange current density decreases appreciably at low temperatures, similar to the values from micropolarization. At low temperatures, the electrolyte containing the DMC once again shows the lowest exchange current density.

### 3.3.3 AC Impedance

The *ac* impedance data were obtained in the frequency range of 100 kHz to 5 mHz at low *ac* amplitude of < 5 mV. Typical impedance plots of graphite electrode in the electrolytes containing DMC, DEC and in the ternary electrolyte at three different temperatures, i.e., 25, 0 and -20°C are shown in the Nyquist or Cole-Cole form in Figs. 5A-5C.

As may be seen qualitatively in the figures, the impedance is high for the DMC-based electrolyte compared to the DEC-based electrolyte at ambient temperature. The trend, however, changes at low temperature, with the DMC-based electrolyte generally showing higher impedance than the DEC-based system. At all the temperatures studied, the ternary solvent mixture provides the least impedance. For a quantitative comparison, the impedance data were analyzed using a generalized equivalent circuit for graphite electrode (insert in Fig. 5).<sup>7-10</sup> The capacitive components are denoted as constant-phase elements (CPE) to describe the depressed nature of the semi-circles.  $R_1$  is ascribed to the sum of the electronic resistance of the electrodes and ionic resistance of the electrolyte. The semi-circle in the high frequency region, represented by  $R_2$  and  $Q_2$  are assigned to the resistance and capacitance of the surface film on the graphite electrode, respectively. The semi-circle in the low frequency region, represented by  $R_3$  and  $Q_3$  is attributed to the reaction (charge transfer) resistance and the double-layer capacitance, respectively. The linear portion (with a angle of 45°), if any, at the (low frequency) end of the spectrum is

related to the diffusional impedance  $W_3$ , denoted by Warburg impedance and is a parallel and/or series combination of diffusional resistance and pseudo-capacitance. The parameters in the equivalent circuit, calculated by a non-linear least square fit using Boukamp method,<sup>11</sup> were listed in Table-3. As may be seen from the Table, the series resistance is the least for DMC-based solutions at ambient temperature. However, at low temperatures, the series resistance goes up due to a fall in the electrolyte conductivity. The film resistance is also the highest for the DMC-based solution. The exchange current density for the Li intercalation reaction, on the other hand, is the lowest for the DMC-based electrolyte solution, especially at low temperatures. The ternary electrolyte shows faster kinetics and lower series and film resistances. In general, the exchange current densities obtained from EIS are higher compared to the corresponding DC values, possibly due to the uncompensated or uncorrected film resistance in the latter.

In addition, the stability of the electrode /electrolyte interface at the graphite electrode in the DMC-based and DEC-based electrolytes during charge-discharge cycling was examined using EIS. In the former electrolyte, there wasn't much change in the interfacial properties, except for a marginal increase in the series resistance. In the DEC-based electrolyte, on the hand, the semi-circle(s) grew considerably, implying an increase in the film resistance as well as the reaction resistance. This suggests that the SEI formed in the DEC-based electrolyte continue to grow even after the (five) formation cycles, whereas in the DMC-based electrolyte, the formation of SEI is nearly complete within five cycles. In other words, the surface films formed in the DMC-based electrolyte provide greater protection against electrolyte reactions as compared to the DEC-based solutions.

### 3.3.4 Current-Voltage Curves

In order to predict the rate capability of graphite anodes in the above three electrolytes, especially at low temperatures, current-voltage curves have been generated on the AA-size cells made in a similar manner with these three electrolytes. These measurements were carried out under near steady-state conditions, i.e., after about 30-60

seconds following current injection.

It may be seen from Fig. 6 that the cell with the ternary electrolyte showed higher voltages than the DEC- based and more noticeably than the DMC-based electrolyte even at 0°C. At lower temperatures, i.e., -20 - -40°C, the effect is more pronounced. These results are thus consistent with the half-cell measurements presented in the earlier sections that the electrode kinetics faster in the electrolyte solutions based on ternary mixture.

### **3.3.5 Discharge Capacity at Low Temperatures**

A number of cells were fabricated with each electrolyte and evaluated in terms of the discharge characteristics and rate capability as a function of temperature. A comparison of the low temperature discharge performance of graphite-based cells at -20°C (Fig. 7) shows that the cells containing the ternary solvent mixture provide the highest capacity at -20°C of ~ 85% of the room temperature capacity, and also with the highest discharge voltages. In comparison, cells with DEC and DMC-based electrolytes yield ~67 and 15%, respectively.

The comparison is more striking at lower temperatures, e.g., -30°C. The ternary ternary solvent mixture permits discharges at temperatures as low as -40 and -60°C, albeit at reduced rates of C/20 and C/150, with yields of 60 % and 80 % (to discharge cut off of 2.0 V), respectively. Fig. 8 illustrates the superior discharge performance characteristics of the ternary solvent system compared to the binary mixtures at different temperatures.

### **3.3.6 Cycle Life Performance**

In addition to evaluating the rate performance as a function of temperature, the cycle life performance was assessed at both room temperature and at -20°C. Although the primary focus of the intended application of planetary probes on Mars is an improvement in the performance at low temperatures, durability under ambient conditions was deemed

necessary during storage, launch, and cruise or during daylight hours on Mars.

Cycling tests under ambient conditions (Fig. 9) reveal that cells containing the ternary solvent mixture have excellent capacity retention of over  $\sim 85\%$  after 600 cycles. The rate of capacity fade during charge-discharge cycling increases as  $\text{EC-DMC} < \text{EC-DMC-DEC} < \text{EC-DEC}$ , which is the same order as the surface film resistance decreases. The rate of capacity fade is  $0.06\%$  per cycle in the DEC-based electrolyte compared to  $0.04\%$  per cycle in the DMC-based and the ternary-solvent-based electrolyte solutions, respectively. It is thus clear that the stronger surface film formed in the DMC-based electrolytes does provide more protection against life-limiting processes such as electrolyte degradation/exfoliation.

At low temperatures, the cycle life is further extended, with a fade rate of  $0.033\%$  per cycle compared (Fig. 10). The cells containing  $1.0\text{ M LiPF}_6$  EC + DMC (30:70) and  $1.0\text{ M LiPF}_6$  EC + DEC (30:70) both showed inferior behavior with lower capacities and higher capacity fade rates, respectively.

### 3.3.7 Self Discharge Characteristics

Self-discharge of a Li ion cell is largely attributed to the delithiation occurring on the graphite anode on open-circuit stand. There could be some degree of self-discharge on the cathode as well, but to a less extent than at the anode. The self-discharge process at the graphite anode could involve reversible solvent reduction conjugate to the lithium deintercalation process. In other words, it could be an indication of the stability of the electrolyte solutions towards the graphite and thus a function of the nature of the solvent, which would in turn dictate the nature of the SEI. It is generally observed that lithium-ion cells containing electrolyte systems which produce poor passivating films on the electrode surfaces, or participate in degradation mechanisms readily, often result in cells with high rates of self-discharge. Self-discharge rates of the graphite electrodes in half-cells containing the above three electrolytes are illustrated in Fig. 11 and are further

substantiated in AA Li ion cells (Fig. 12). Self-discharge rates in the latter are measured as the capacity that needs to be injected into the cell, after for six months of storage at 0°C, to bring it to fully charged state. As shown in Figs 11-12, the self-discharge rate increases as  $\text{EC} + \text{DMC} (30:70) < \text{EC} + \text{DMC} + \text{DEC} (1:1:1) < \text{EC} + \text{DEC} (30:70)$  electrolyte. These results suggest that the DMC-based electrolyte solutions enable the formation of the more stable and protective surface films compared to the DEC based electrolyte, with the ternary mixture displaying intermediary behavior.

#### 4.0 Conclusions

The cycle life and rate capability of Li ion cells are guided by the stability and the charge transfer characteristics of the surface films on graphite anodes. Electrolyte conductivity, which is a pre-requisite for the desired performance at low temperature, is maximum for electrolytes based on equi-proportion ternary mixture of EC, DEC and DMC solvents compared to either (EC-) DMC or DEC based solutions. In addition, the interfacial properties in the ternary mixture are more favorable to Li intercalation-deintercalation kinetics, especially at low temperature. As summarized qualitatively in Table-3, among the three electrolytes studied, the film resistance increases with increasing DMC content. Also, the protective nature of the films during formation cycles, charge-discharge cycling or open-circuit stand is the highest in the DMC-based electrolyte, as evident from the lowest irreversible capacity, capacity fade and self-discharge. The kinetics of Li intercalation-deintercalation, on the other hand, are adversely affected, especially at low temperature, possibly due to a contribution from the tenacious surface film. All things considered, the ternary solvent system seems to provide excellent low temperature performance combined with adequate durability under ambient conditions and thus constitutes a suitable electrolyte for the Mars Exploratory missions. This may partly be attributed to the in-situ formation via disproportionation of ethyl methyl carbonate (EMC),<sup>12-13</sup> which by itself is a good co-solvent for low temperature applications.

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## 7.0 Figure Captions

Fig. 1 : Conductivity of lithium ion battery electrolyte solutions containing 1M LiPF<sub>6</sub> dissolved in 1) EC-DMC (30:70), 2) EC-DEC (30:70) and 3) EC+DMC+DEC (1:1:1) solvent mixtures.

Fig. 2 : Potentials of graphite electrode during first lithiation–delithiation cycle in 1M LiPF<sub>6</sub> in 1) EC-DMC (▲), 2) EC-DEC (◆) and 3) EC+DMC+DEC ) (●) solvent mixtures.

Fig. 3 : Typical DC micropolarization plots of graphite anode in electrolytes containing 1M LiPF<sub>6</sub> in 1) EC+DMC (30:70) 2)EC+ DEC (30:70) and 3) EC+DMC+DEC (1:1:1).

Fig. 4 : Tafel plots of Li deintercalation process from graphite in electrolytes containing 1M LiPF<sub>6</sub> in 1) EC-DMC, 2) EC-DEC and 3) EC-DMC-DEC (1:1:1) at A) 25, B) 0 and C) –20°C.

Fig. 5 : Electrochemical Impedance Spectroscopy (EIS) plots (Nyquist) of graphite in electrolytes containing 1 M LiPF<sub>6</sub> in 1) EC-DMC, 2) EC-DEC and 3) EC-DMC-DEC (1:1:1) at A) 25°C, B) 0°C, and C) -20°C.

Fig. 6 : Comparison of current–voltage curves of AA Li ion cells with electrolyte based on 1) EC-DMC, 2) EC-DEC and 3) EC+DMC+DEC solvent mixtures at A) 25, B) 0, C) –20

and D)  $-40^{\circ}\text{C}$ , respectively.

Fig. 7 : Comparison of the discharge curves of graphite-based AA-size lithium ion cells at  $-20^{\circ}\text{C}$  as a function of electrolyte.

Fig. 8 : Comparison of the low temperature performance characteristics of graphite-based AA-size lithium ion cells with electrolytes based on EC-DMC, EC-DEC and EC+DMC+DEC solvent mixtures at C/20 and different temperatures.

Fig. 9 : Cycle life of Li-ion cells with 1)EC-DMC, 2) EC-DEC and 3) EC-DMC-DEC based electrolytes at  $25^{\circ}\text{C}$ . Cells were charged at rate of 50mA ( $\sim\text{C}/10$ ) and discharged at a rate of 100mA ( $\sim\text{C}/5$ ).

Fig. 10 : Cycle life of Li-ion cells with 1) EC-DMC, 2) EC-DEC and 3) EC-DMC-DEC based electrolytes at  $-20^{\circ}\text{C}$ . Cells were charged at rate of 25mA ( $\sim\text{C}/20$ ) and discharged at a rate of 50mA ( $\sim\text{C}/10$ ).

Fig. 11 : Self-discharge of graphite electrodes in electrolytes containing 1 M  $\text{LiPF}_6$  in 1) EC+DMC (30:70) 2)EC+ DEC (30:70) and 3) EC+DMC+DEC (1:1:1).

Fig. 12 : Self-discharge of Li-ion AA cells with 1) EC-DMC, 2) EC-DEC and 3) EC-DMC-DEC based electrolytes, in terms of charge acceptance after prolonged storage.



Table 1: Physical properties of organic carbonate solvents commonly used in rechargeable lithium-ion cell technology.

	Visc. $\eta$ (cP, 25°C)	Dielect. Const. $\epsilon$ (25°C)	Donor Number $D_N$	M.W.	Melting Point	Boiling Point	Density
<b>Ethylene carbonate</b> (1,3-dioxolane-2-one)	1.85 (400C)	89.6 (400C)	16.4	88.06	38°C	243°	1.321
<b>Dimethyl carbonate</b> (DMC)	0.585	3.12	NA	90.08	3°C	90°	1.069
<b>Diethyl carbonate</b> (DEC)	0.748	2.82	NA	118.13	-43°C	127°	0.975

Table 2 : Specific reversible and irreversible capacities of graphite Anode in Li ion cells containing EC-based electrolytes.

Electrolyte Type (All contain 1.0 M LiPF <sub>6</sub> )	Reversible Capacity (mAh/g)		Irreversible Capacity (mAh/g)	
	Cell 1	Cell 2	Cell 1	Cell 2
EC + DMC + DEC (1:1:1)	Cell 1	Cell 2	235.36	82.16
			217.97	72.30
EC + DEC (30/70)	Cell 1	Cell 2	200.73	111.90
			215.31	139.49
EC + DMC (30/70)	Cell 1	Cell 2	221.86	47.18
			261.57	48.91

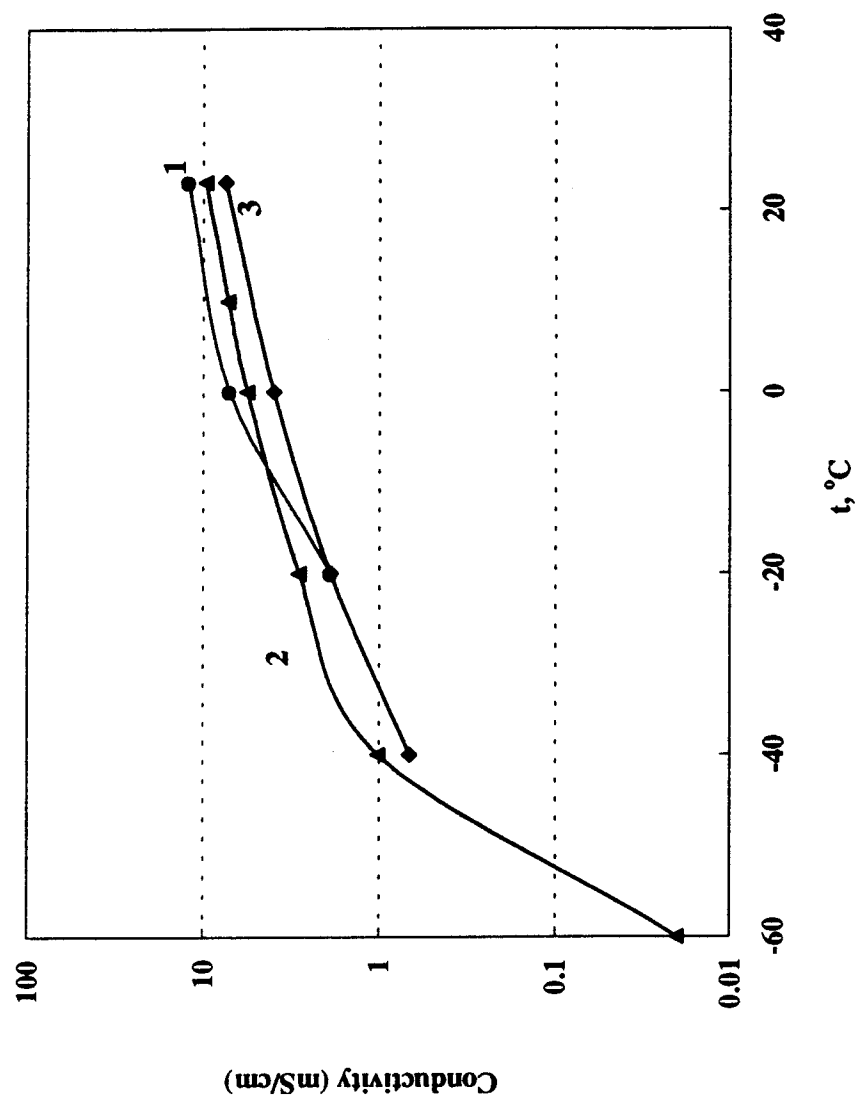
Table 3 : Kinetic parameters for Li deintercalation reaction in EC-based solvent solution.

Solvent	Temp, °C	Micropol Exchange c.d mA/cm <sup>2</sup>	Tafel		AC Impedance		
			Exchange c.d mA/cm <sup>2</sup>	Trans Coef	R <sub>s</sub> , Ω.cm <sup>2</sup>	R <sub>f</sub> , Ω.cm <sup>2</sup>	Exchange c.d., mA.cm <sup>-2</sup>
<b>EC-DMC</b>	25	0.22	0.082	0.45	5.5	57.1	5.89
	0	0.044	-	-	9.7	441.2	1.76
	-20	0.022	-	-	60.3	815.3	0.33
<b>EC-DEC</b>	25	0.282	0.44	0.60	9.1	52.2	7.99
	0	0.06	-	-	13.3	170.3	1.19
	-20	0.033	0.0014	0.65	38.1	305.7	0.76
<b>EC-DMC-DEC</b>	25	0.279	0.38	0.58	8.8	30.9	6.81
	0	0.108	0.024	0.343	12.6	113.5	1.68
	-20	0.033	0.0028	0.69	13.5	358.6	0.70

**Table 3 : Qualitative comparison of performance characteristics of electrolytes based on EC-DMC, EC-DEC and EC-DMC-DEC**

<b>Characteristic</b>	<b>EC-DMC</b>	<b>EC-DEC</b>	<b>EC-DMC-DEC</b>
Electrolyte conductivity at low temp.	Low	High	High
Film Resistance	High	Low	Intermediary
Durability (Cycle Life)	High	Low	Intermediary
Li intercalation kinetics at LT	Low	High	High
Irreversible Capacity	Low	High	Intermediary
Self Discharge	Low	High	Intermediary
Performance at LT	Low	Intermediary	High

Fig. 1



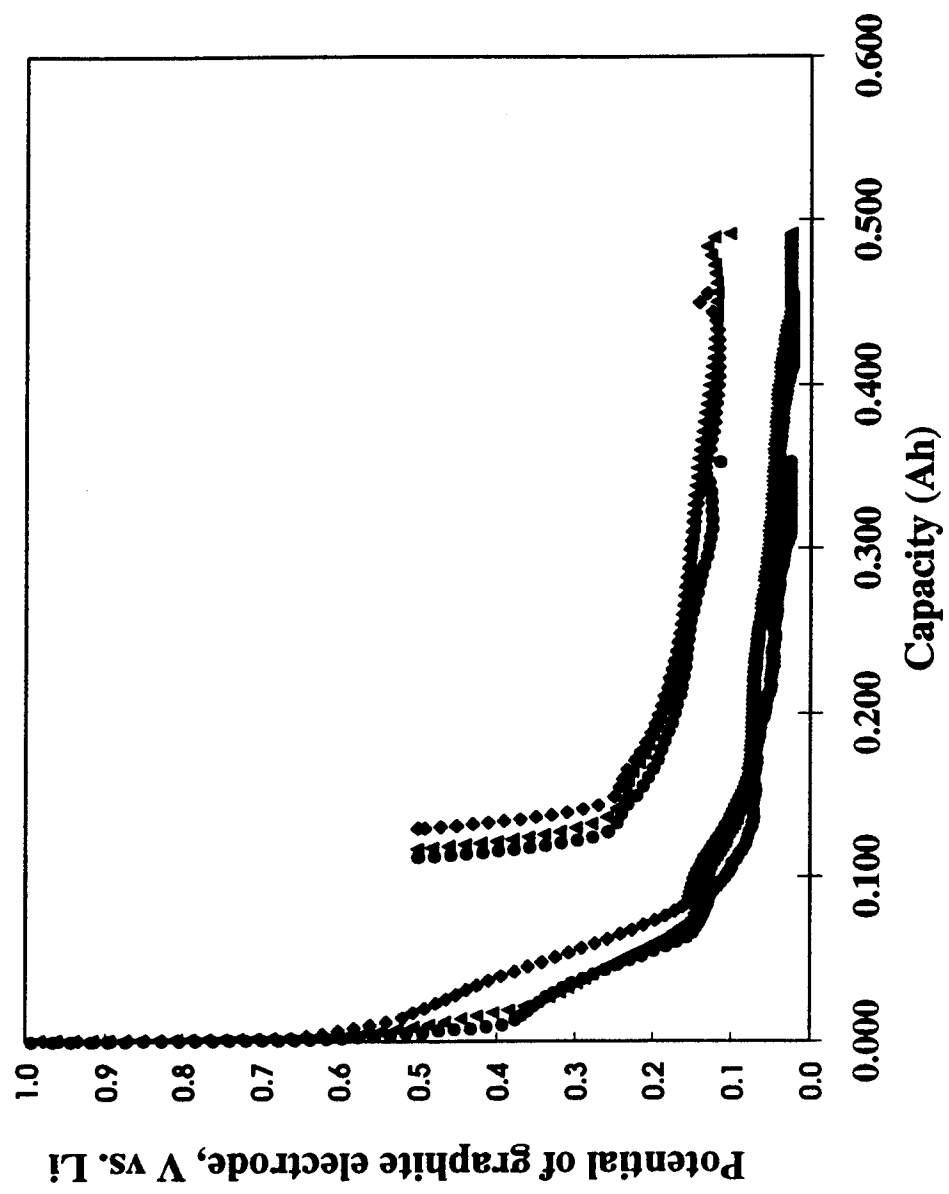
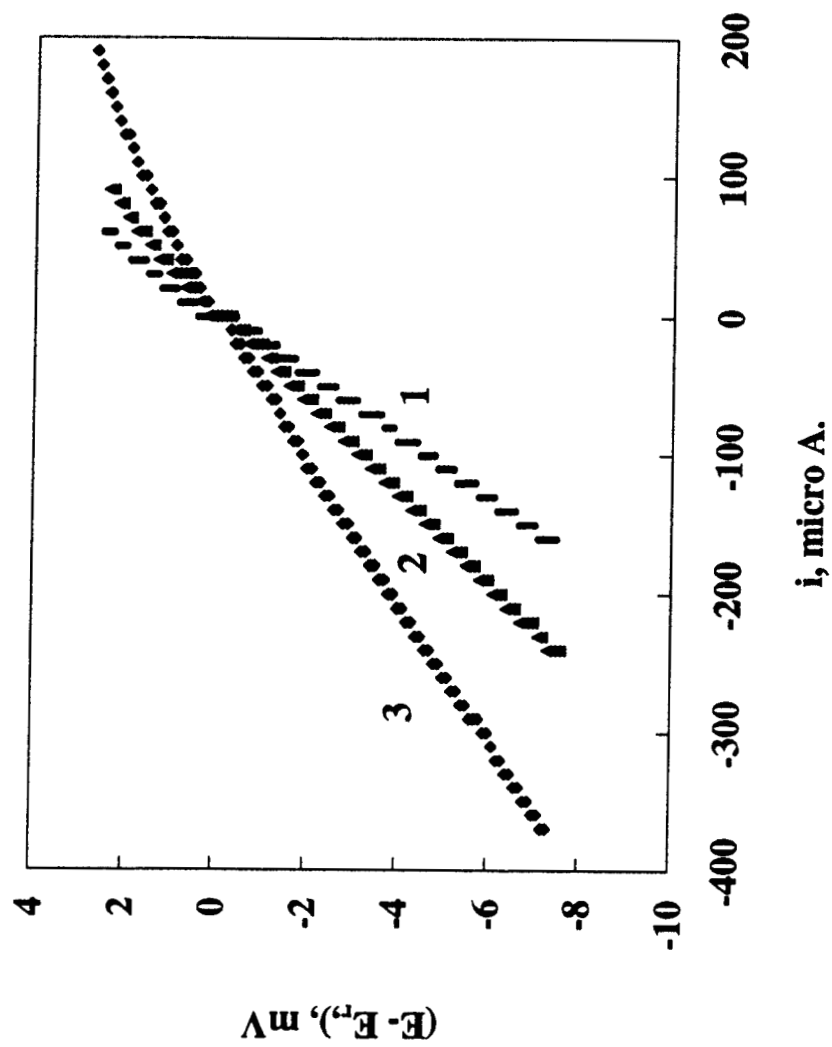


Fig. 2

Fig.3



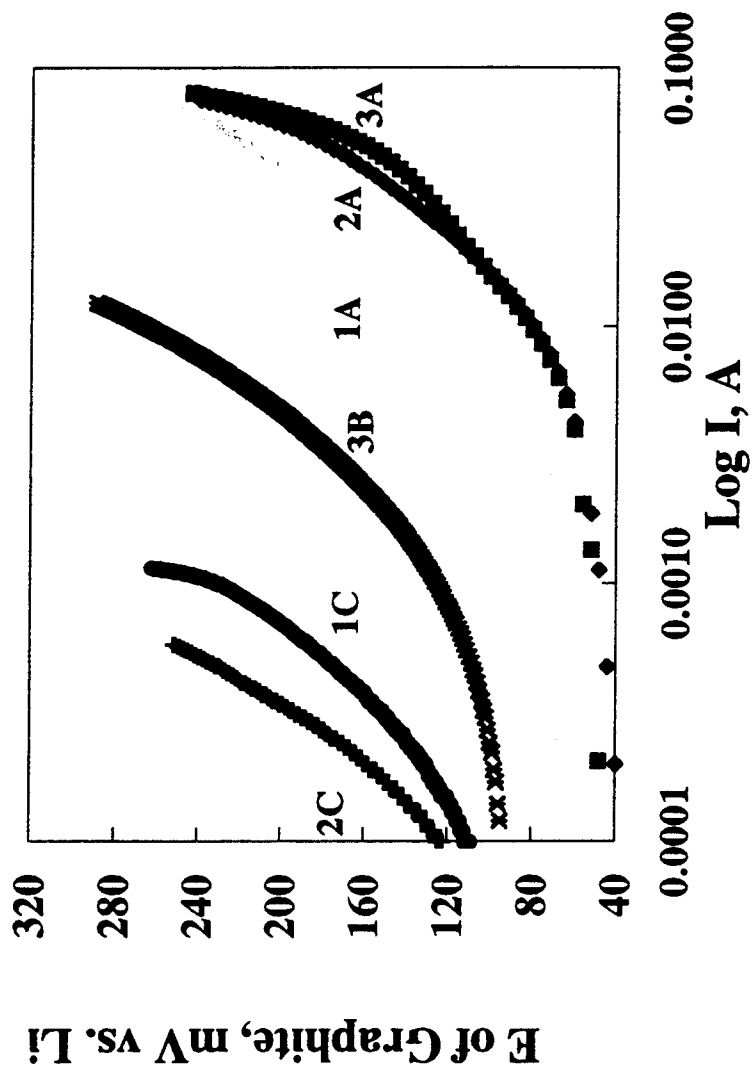
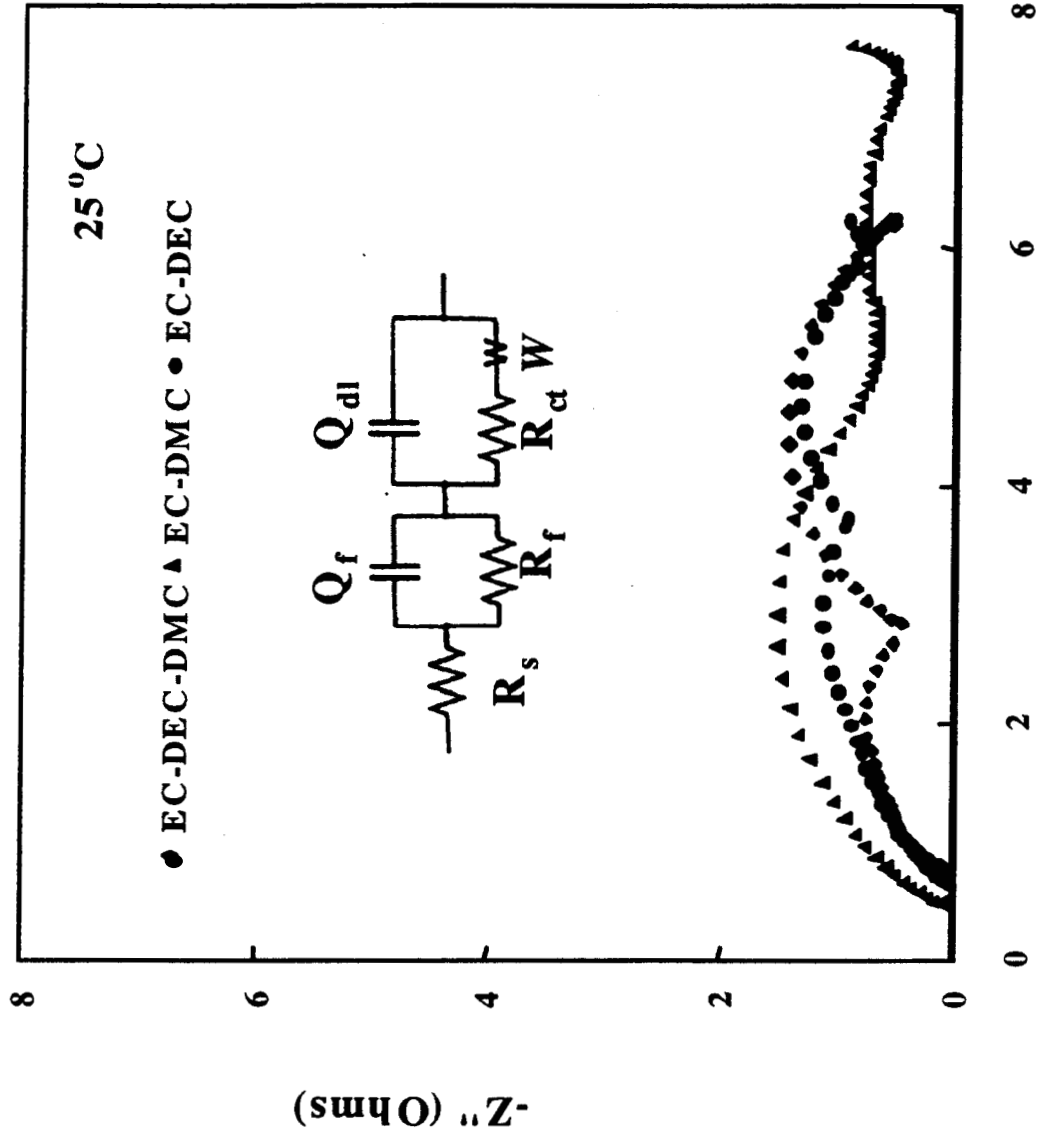


Fig. 4



5 A



Z' (Ohms)

Fig. 5B

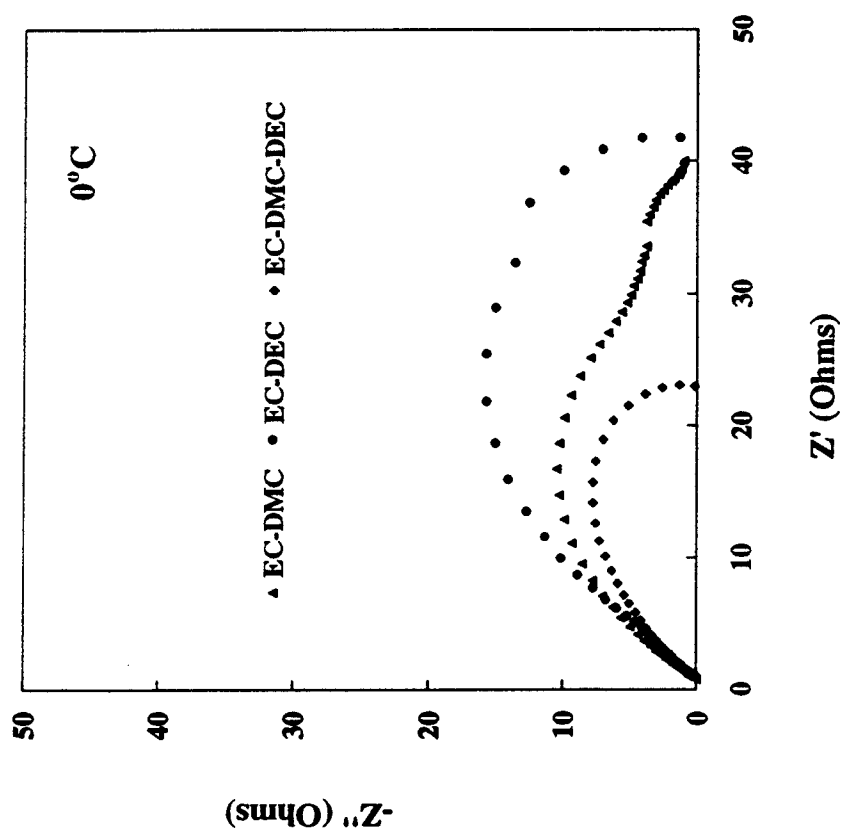


Fig. 5c

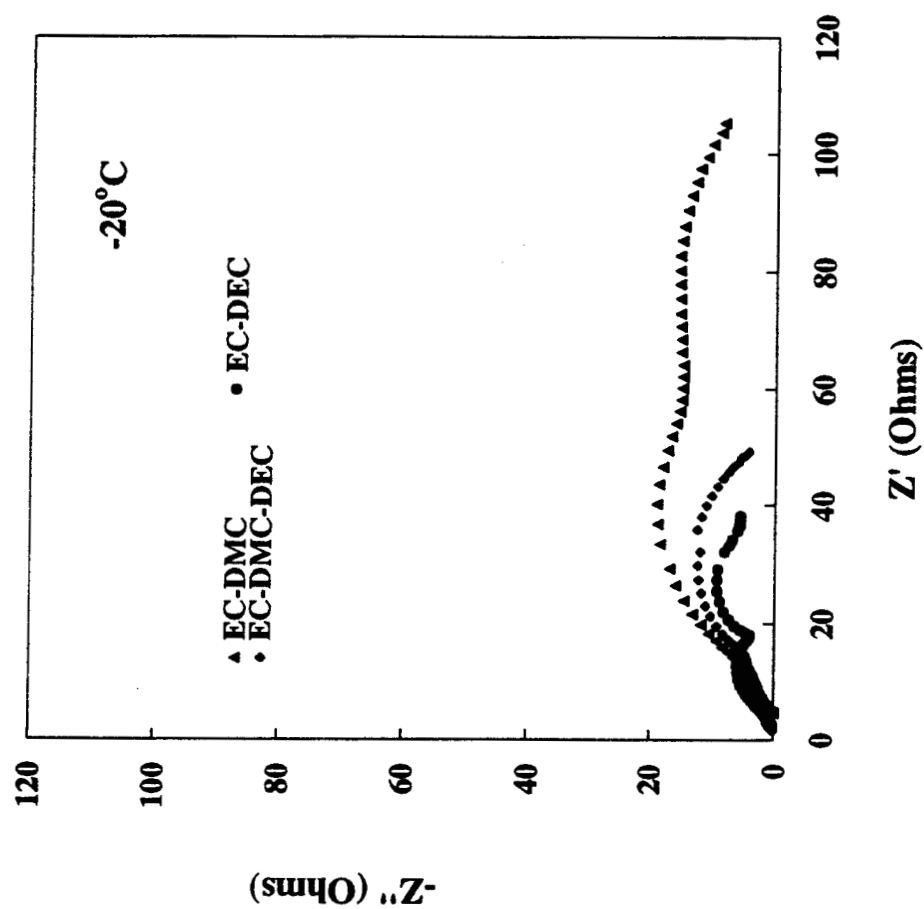


Fig. 6

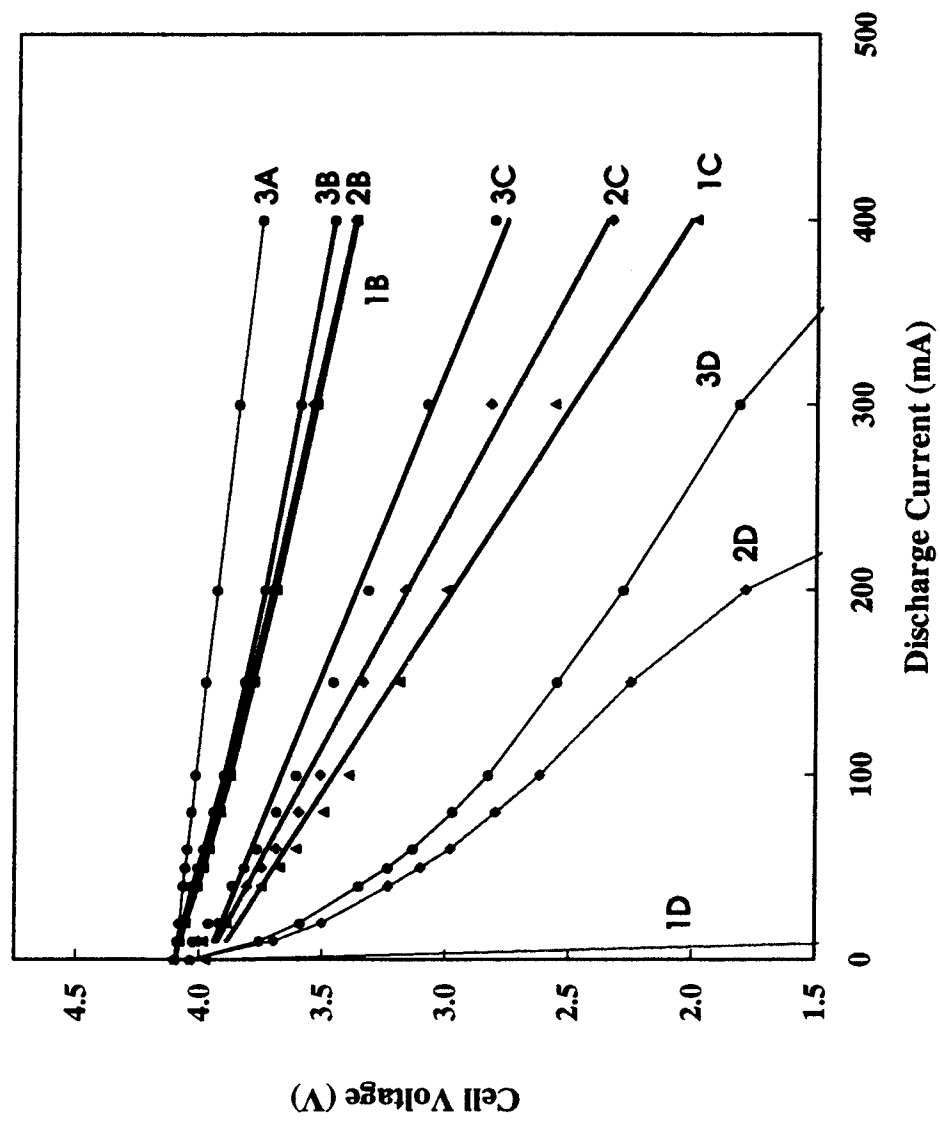


Fig. 7

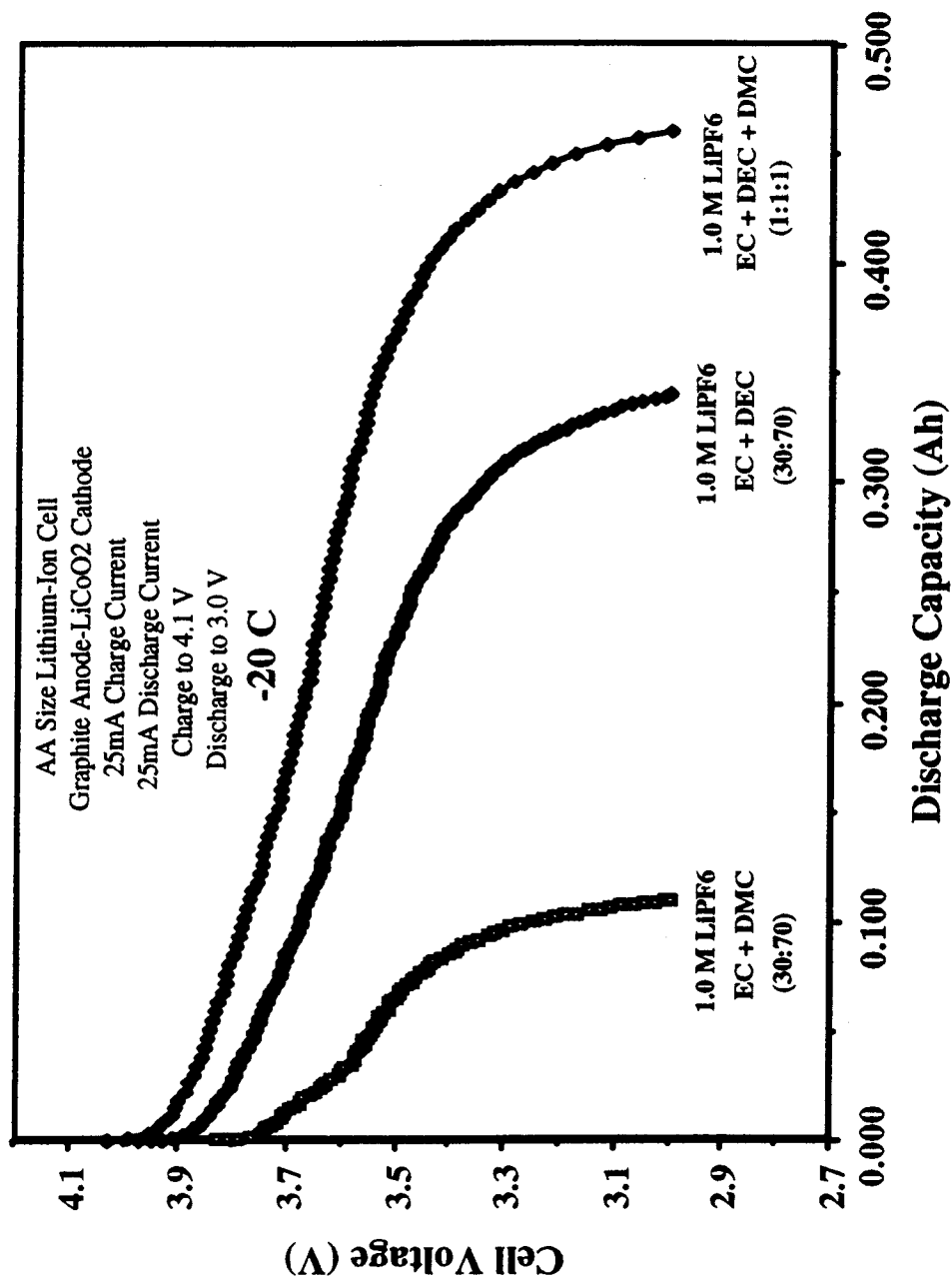


Fig. 8

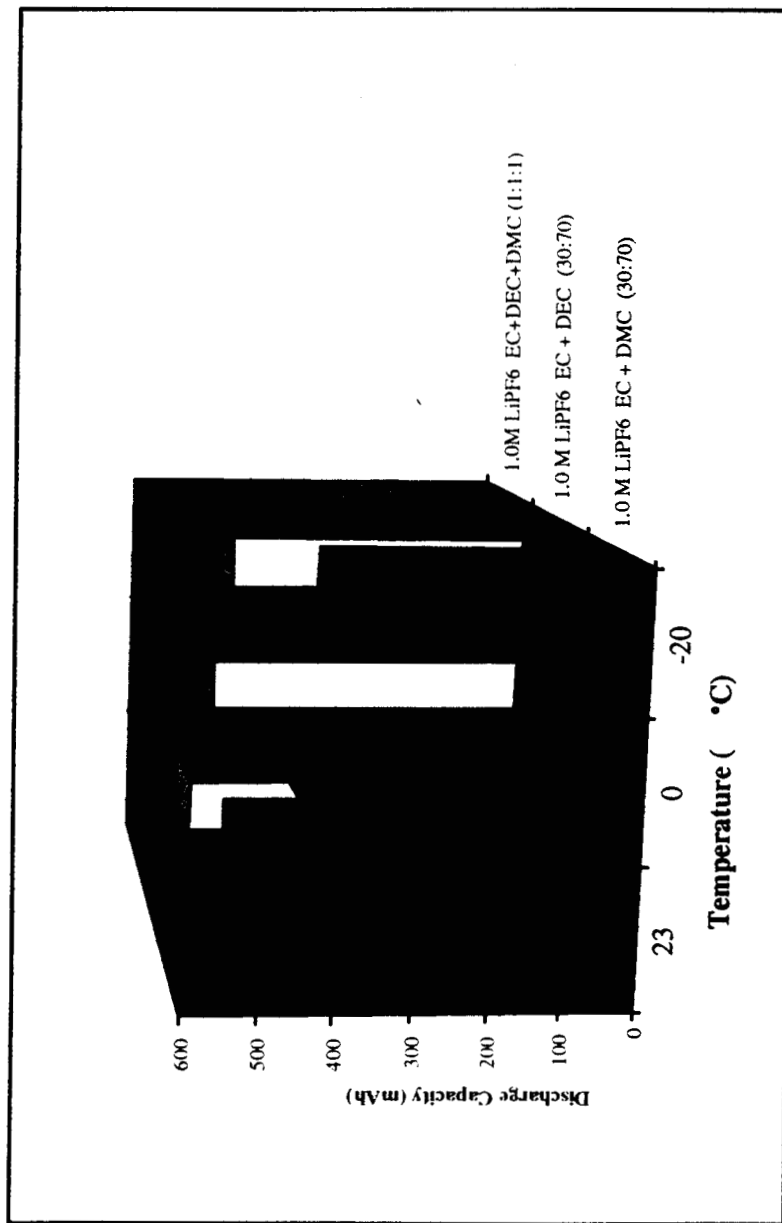


Fig. 9

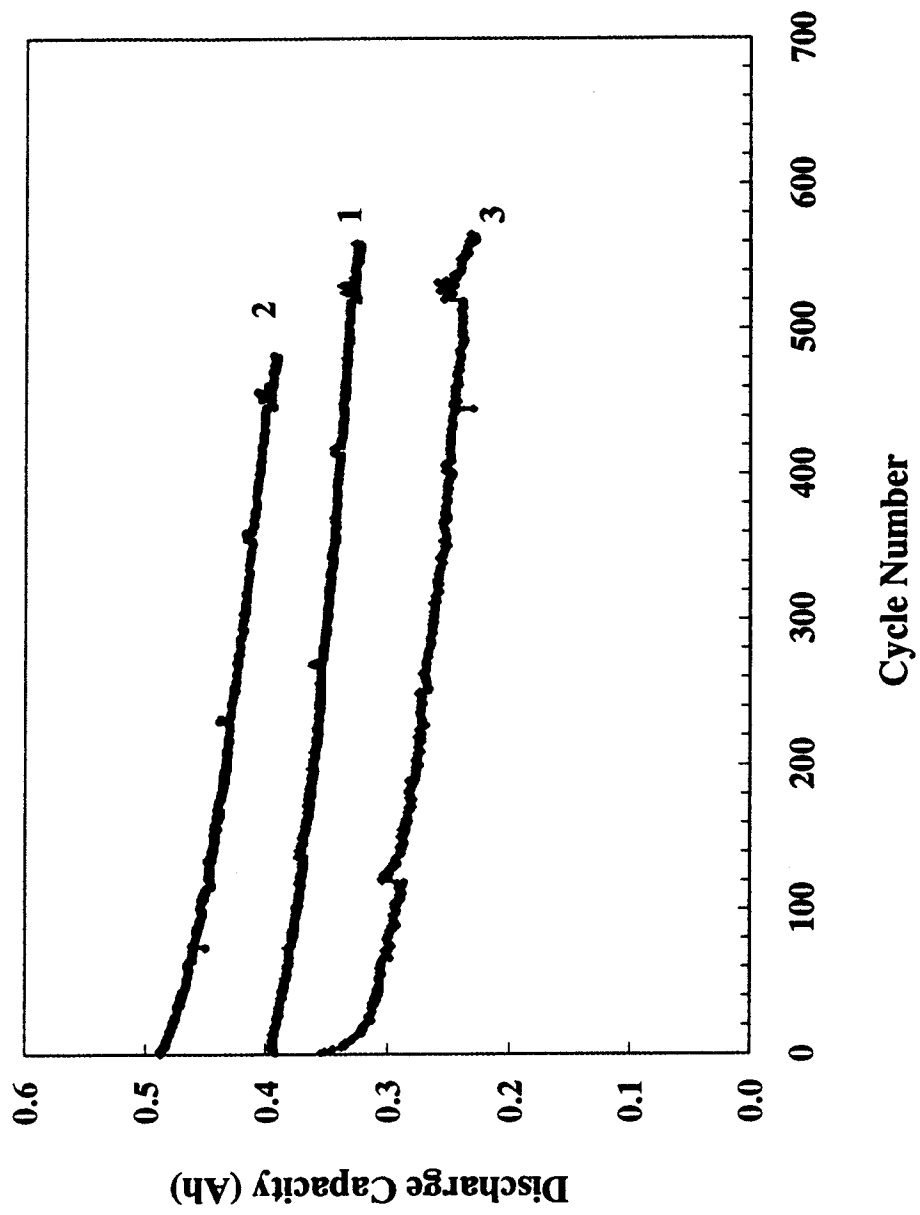


Fig. 10

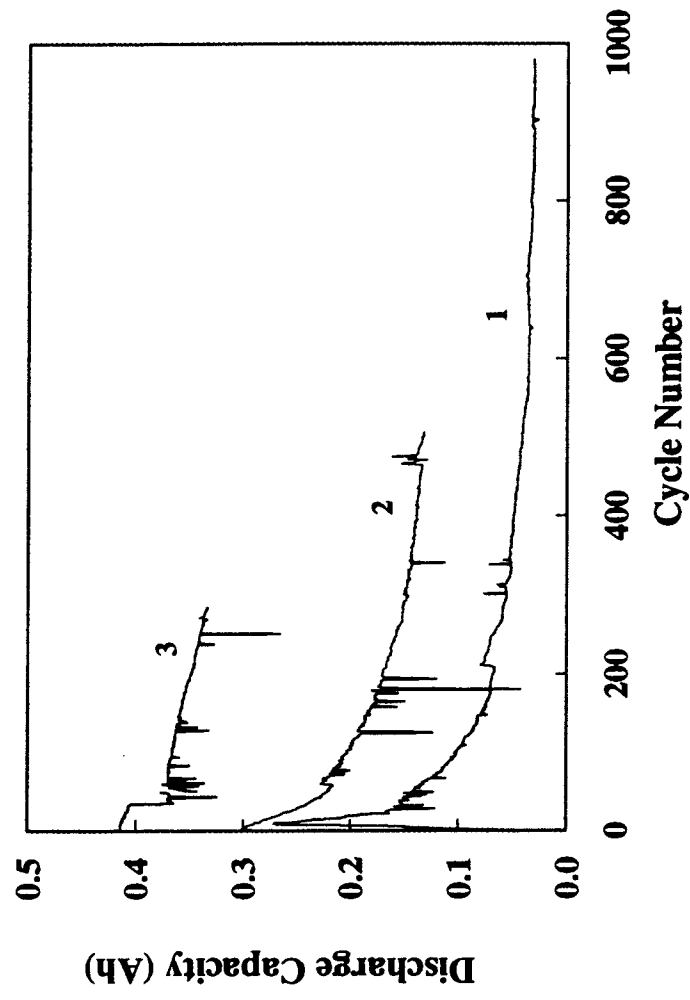




Fig. 11 :

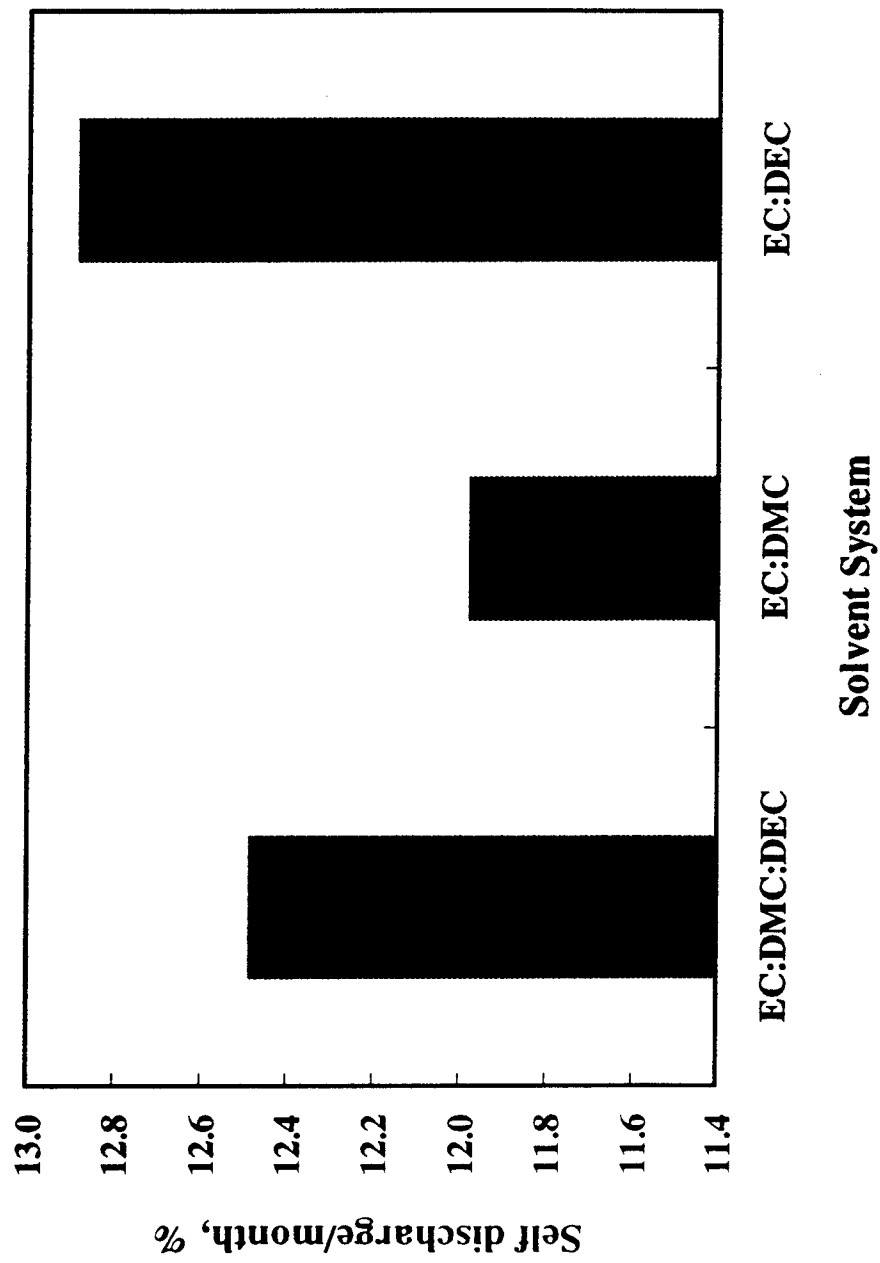


Fig. 12

